Influence of α_s precipitates on electrochemical performance and mechanical degradation of Ti-1300 alloy

Jinwen Lu [a*], Xirong Yang [b], Yongqing Zhao [a*], Longlong Dong [a], Yongqing Fu [c], Yan Du [a], Wei Zhang [a], Yusheng Zhang [a]

[a] Advanced Materials Research Central, Northwest Institute for Nonferrous Metal Research, Xi'an 710016, China

[b] School of metallurgical Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China

[c] Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, UK

Abstract: The influence of α_s precipitates on electrochemical behavior and mechanical degradation of Ti-1300 alloy in artificial seawater have been studied. The results show that corrosion resistance and mechanical degradation have been significantly affected by the formation of acicular α_s precipitates. The precipitated α_s phase with an acicular shape around 40 ~ 60 nm in width are uniformly distributed inside β grain. Many α_s precipitates are intersected each other and keep a well-defined Burgers orientation relationship with β matrix, which restricts the growth of other α_s phases due to pinning effect. Within the electrolyte, the α_s phases can form "microgalvanic cells" with their adjacent intergranular β phases, which dramatically deteriorate its corrosion resistance. The mechanical properties of the alloy are also degraded with the increase of immersion time due to the pitting reaction. The precipitated microstructure exhibits an inferior mechanical degradation behavior, and this is mainly because a lot of corrosion cavities are nucleate d and propagated at the interface between α_s precipitates and prior β grains.

Keywords: Titanium, Passive film, Pitting corrosion, Mechanical degradation performance

1. Introduction

Owing to their high specific strength, excellent workability, and outstanding corrosion

* E-mail address: lujwen@163.com(Jinwen Lu), trc@c-nin.com (Yongqing Zhao)

resistance, metastable β titanium (Ti) alloys have been extensively used in aeronautics, petrochemical and nuclear industry [1-3]. It is well known that titanium and its alloys can rapidly react with oxygen molecules in electrolyte and form a protective oxide layer with a thickness of several nanometer [4-6], which provides a good corrosion resistance. Comparing with α or α+β Ti alloys, β Ti alloys not only have excellent mechanical properties due to the precipitation of primary/secondary α phases (e.g., α_p and α_s) after thermomechanical processing, but also improves corrosion resistance due to the formation of the massive β elements oxides [7]. The service life of β Ti alloys is dependent on their corrosion behavior, and it was reported that their metallurgical defects and different service environments (such as those in chemical and marine industries) cause various types of corrosion damages [8, 9]. According to literature [10-12], the formed passive protective layer can be gradually in the electrolyte due to the concentrated corrosive ions (such as F^- and Cl^-), and pitting corrosion appears after the oxide layer is destroyed [8, 13]. This process can be explained by the preferred adsorption of corrosive ions [9]. Excessive metallic ions released by leaching or synergetic effects of corrosion reaction and mechanical loading, can significantly increase stress corrosion fracture and decrease the fatigue strength of the alloy. Therefore, it is critical to find a way to improve the corrosion resistance for Ti alloy.

It is well known that corrosion resistance and passivation behavior of Ti alloys are relied on the microstructures and relative density of passive layer [13, 14]. Some studies [15-17] reported that the passive film formed on Ti alloy surface is mainly composed of titanium oxide (TiO_2), and also a small amount of suboxides (TiO and Ti_2O_3). This passive film exhibits a bi-layer structure, e.g., an inner barrier layer at the metal/oxide interface and an outer porous layer at the solution/oxide interface, and the stability of passive film is dominated by the inner barrier layer

[14, 17, 18]. In addition, some researchers have also investigated corrosion behavior of Ti alloys with the addition of different alloying elements [16-20]. It is found that two types of alloying elements can effectively inhibit local breakdown or dissolution of passive film. The first type is cathodic alloying elements [19, 20], with their representative elements of platinum-group metals (such as Pd, Pt, Ni and Ru). The enhancement of corrosion resistance is mainly due to the acceleration of cathodic reactions, which can change the corrosion potential to a critical value in passive region, thus resulting in lower passive current densities and improving passivity [10]. The second type is anodic alloying elements, which can reduce thermodynamic instability and anodic activity of Ti alloy [18, 21, 22]. The representative elements are Mo, Ta, Zr, V, Cr, Nb, etc [5, 23, 24]. Li [15], Bai [18] and Yu [25] reported the effects of Zr, Nb, Mo and Ta alloying on corrosion properties of Ti alloys. It was reported that passive film is composed of several different oxides, including TiO_2, Nb_2O_5, ZrO_2, MoO_2 and Ta_2O_5 [9]. These oxidates can enhance the integrity and the stability of the passive film, thus improving the resistance of titanium alloys due to the formation of a strong covalent bond with neighboring Ti, Zr, Ta and Nb atoms through sharing of d level electrons [9].

In addition, the microstructure is also a key factor to influence the corrosion performance of β Ti alloys [13]. Some studies showed that the α+β interphase acted as a preferential dissolution locations to trigger the pitting reaction [5, 13]. However, there are still a lot of unsolved problems for improving the corrosion performance of Ti alloy. For example, in oxidizing environments such as nitric acid solutions, Ti alloy can spontaneously form a compact passive film, which protects the matrix [26, 27]. By contrast, in reducing environments such as hydrochloric acids, Ti alloys present relatively poorer corrosion resistance due to the influence of corrosive ions (such as F^- and

Cl^-) on the anodic process [11, 19, 28, 29].

In the present work, the effects of nano-precipitates of α_s phase on passive behavior and corrosion performance of Ti-1300 alloy is studied in artificial seawater with different pH values, and the degradation of mechanical properties after different immersion times is also investigated by using tensile testing method with a slow strain rate. The corrosion mechanism is discussed based on surface analysis and microstructural characterization.

2. Experimental

2.1 Material

Ti-1300 alloy used in this study was fabricated by vacuum consumable arc-remelting furnace under an argon protection atmosphere. The ingots were re-melted three times to ensure chemical homogeneity. They were then hot forged at 950 °C into square-shaped billets with 50mm in all dimensions. Finally, the circular rods with a diameter of 11 mm were obtained by hot rolling at 750 °C. Compositional optimization was performed using First-principles calculations in Ti-Al-X system with β-stabilizing elements in order to achieve superior mechanical properties. The chemical composition was tested as following (in *wt*. %): 5.15 Al, 2.96 Zr, 3.96 Cr, 3.79 Mo and 3.95 V with the balance Ti, as measured by Inductively coupled plasma massspectrometry (ICP-MS). The α/β phase transition temperature determined by the standard metallographic method was approximately 830 °C. The details of quantitative metallography are as follows: cylindrical specimens (Φ11 mm × 10 mm) were cut from circular bars and were solution treated at various temperatures, both above and below the α/β phase transition temperature and examined metallographically. The specimens were solution-treated in the temperature range of 800 - 860 °C for 1 hour in an electric furnace and then water quenched to examine the microstructure

(metallographic techniques). The α/β phase transition temperature was identified from the cross-section microstructure analysis. When the solution temperature was above 830 °C, the microstructure was a pure β phase. Therefore, the α/β phase transition temperature of the alloy was identified to be 830 ± 5 °C. The equiaxed microstructure was obtained by solution treated at 870 °C for 1h and air cooling, and the precipitated microstructure was achieved by the single β phase solution and aging treatment (treated at 500 °C for 6 hours and air cooled at ambient temperature).

2.2 Microstructural characterization

Microstructural characterization was performed using an optical microscope (OM, Leica MPS 30), scanning electron microscope (SEM, JSM-6700, Japan) and transmission electron microscope (TEM, JEOL, JEM-2100). The specimens for OM and SEM were polished using the 2000 grid SiC paper, then etched in a Kroll's reagent (1 vol. % HF, 3 vol. % HNO_3, and 5 vol. % H_2O), and ultrasonically cleaned in ethanol and distilled water in sequence. The thin TEM foils were electropolished using a twin-jet technique in a solution of 10 % perchloric acid and 90 % methanol at a voltage of 30 V and a temperature of -35 °C. Crystalline phase analysis was performed using by X-ray diffraction (XRD) analysis with Cu-Kα radiation source operated at 30 kV and 300 mA (XRD, D8, ADVANCE). The microstructural analysis (such as volume fraction, grain size and length-width ratio) of α_s precipitates was carried out by using the image analysis software of Image J. To investigate the compositions of the passive films and chemical states of the alloying elements, X-ray photoelectron spectroscopy (XPS) analysis was performed on the film after its immersion in the artificial seawater solutions for 24 hours.

2.3 Electrochemical measurements

Electrochemical measurements were carried out with an IM6 Zahner-electrik Gmbh (Zenniom, Germany) electrochemical workstation. A conventional three-electrode system was adopted using a saturated calomel electrode (SCE) as the reference electrode and a platinum plate (15mm×15mm) as the counter electrode, and the measured sample with a certain exposed area (0.95 cm^2) as the working electrode. Artificial seawater solutions with different pH value were used as electrolyte, and their compositions are listed in Table 1 [30]. The pH value in the electrolyte was adjusted by adding different HCl (1 M) or NaOH (1 M) solutions. Prior to the electrochemical tests, the samples were immersed in the electrolyte to obtain a stable corrosion potential. Open circuit potential (OCP) measurement was conducted for 60 min, which started from the moment when the electrode was immersed into the electrolyte. Potentiodynamic polarization (PP) tests were performed in the range from -1 V to 2 V at a scan rate of 0.5 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were carried out under the potentiostatic condition at OCP with a 10 mV amplitude AC voltage signal, and the applied frequency range was from 10^5 Hz down to 10^{-1} Hz. The obtained EIS spectra were fitted using the Zsimpwin software. Each test was performed three times with a fresh solution and a new specimen at 25°C± 0.5 °C.

2.4 Immersion tests

Immersion tests were performed in a 5 M HCl solution at 25 °C. The specimens (Φ11 mm × 5 mm) were cut and ground using 2000 grit SiC paper, and then cleaned ultrasonically with acetone and deionized water. This cleaning protocol was same for the electrochemical samples. During immersion tests, the specimens were immersed in 450 ml HCl solutions under the ambient environment, and the solution was removed every 2 days over a 10 days immersion period. In

order to verify the validity of immersion result, immersion test of each sample was repeated twice, and the experimental data was accordingly obtained from the average of two immersion results. The morphology of the corroded surface after different immersion periods was examined using SEM (JSM-6700, Japan).

2.5 Mechanical tests

Mechanical properties of Ti-1300 alloy were studied using a slow strain rate testing (SSRT) method in 5 M HCl solution at 25 °C. The standard cylindrical tensile specimen with a gage length of 25 mm and a cross section diameter of 5 mm was used in this study, and a strain rate of 1×10^{-5} mm/s was applied until the fracture of the sample. In order to confirm the validity of tensile test results, tests of each condition was repeated twice, and the ultimate tensile strength, yield strength, and elongation were obtained from the average of two tensile results. After the tensile test, the fracture surface was cleaned ultra-sonically, and then observed using SEM (JSM-6460, Japan) to identify the fracture mode.

3. Results and discussion

3.1 Microstructural characterization

Fig. 1(a) shows XRD results of Ti-1300 alloys with different microstructures, which show that the phase composition for precipitated microstructure is consisted of α and β phases, but only β phase can be detected for equiaxed microstructure. The clear evidence for the phase variations is the differences of the reflection peak near 2θ = 40.5° for α_s phase, which has the same crystal structure with α phase. In addition, the (110) peak of β phase (near 2θ = 38.5°) is broadened and its intensity becomes weakening with the precipitation of α_s phase. This phenomenon clearly indicates that the volume fraction of β phase decreases with the precipitation of α_s phase [31].

Fig. 1(b) and Fig. 1(c) show the OM micrographs of Ti-1300 alloy with equiaxed and precipitated microstructures, and the higher magnified SEM image for precipitated microstructure is given in Fig. 1(d). It shows the equiaxed β grains with an average grain size of approximately 73.05 μm (Fig. 1(b)). This microstructure is typical character for Ti alloys within the single β region (e.g., above α/β phase transition temperature), which means that the recrystallization of the deformed grains has fully completed [32]. As can be seen from Fig. 1(c), the precipitated microstructure consists of acicular α_s precipitates and intergranular β phase. Moreover, the prior β grain boundaries are straight and clear, and the primary β grain size is around 87.82 μm, indicating that the recrystallization for prior β grain occurred [32]. As shown in Fig. 1(d), the acicular shape α_s phases around 40 ~ 60 nm in width are uniformly distributed into prior β grain, and their average volume fraction and length-width ratio are 19.50 % and 13.11, respectively.

Fig. 2 shows bright and dark field TEM micrographs of the acicular α_s precipitates, inset shows their corresponding diffraction pattern. Fig. 2(a) shows that the precipitated microstructure consists of acicular α_s platelets uniformly distributed inside the β phase matrix, and selective area diffraction (SAD) patterns confirm the presence of α_s platelets. Acicular α_s phases (bright fine acicular shape) are homogeneously precipitated in β matrix (darker contrast), and which can be seen from the dark-field micrograph as shown in Fig. 2(b). Many α_s platelets mutually intersect each other, and the other precipitates within β matrix along a specific habit plane, which restricts the mobility of prior β grain boundaries and the growth of other α_s phase due to the significant pinning effect. Moreover, the α_s platelets have Burgers orientation relationship with the adjacent β matrix (shown in Fig. S1), and the lath size of the α_s platelets is dependent on the diffusion of atoms cross the boundary during thermal treatment process. This result is consistent with the work

by Chen [33] and Huang [34]. In addition, the precipitated α_s phases are the key strengthening phase for Ti-1300 alloy, which has been reported in our previous work in details [22]. Therefore, precipitation strengthening has been considered to the main strengthening mechanism for Ti-1300 alloy.

3.2 Electrochemical corrosion behavior

3.2.1 OCP test

Fig. 3(a) and Fig. 3(b) show the OCP results for equiaxed and precipitated microstructures as a function of immersion time in artificial seawater with different pH values. The dependence of the stable OCP on pH value is shown in Fig. 3 (c). When the pH value is lower than 7.5, the OCP evolution curves for both microstructures show a typical passivation characteristic, e.g., the OCP increases rapidly with immersion time in the first 300 s, but then reaching a near-steady-state. These are linked to the spontaneous formation and growth of oxide layers. Referring to *E*-pH diagrams [35], the OCPs fall within the passivation region. Similar phenomenon of spontaneous passivation for β Ti alloys has previously been reported by Nakagawa [19]. When the pH value is increased to 9.54, OCPs for both microstructures decrease rapidly during the initial immersion period (approximately 350 s) and stabilize at relatively lower potentials, which is probably associated with the formation of less stable and non-effectively protective oxide layers [36].

In addition, the OCP for precipitated microstructure in the artificial seawater remains a relatively low steady-state potential when compared with that for the equiaxed microstructure (Fig. 3(c)), implying the generation of an unstable passive layer due to α_s platelets. Previous studies [17, 37] showed that the passive film on Ti surface was mainly composed of TiO_2 and Ti suboxide (such Ti_2O_3 and TiO), TiO_2 was the dominant portion of the outermost layer, the lower oxidation

states Ti_2O_3 and TiO were mainly formed at the metal-oxide interface as an inner barrier layer. The OCP was the potential in the stabile region of this oxides, and the corrosion resistance was controlled kinetically by the stability of the passive film [9]. For precipitated microstructure, α_s phase acts as the preferential dissolution locations due to the formation of microgalvanic cells between α_s platelets and adjacent intergranular β phase, and the testing results show that α_s phase decreases the stability of the passive film. The similar conclusions have been obtained in the literature [23, 38].

3.2.2 PP measurement

Fig. 4(a) and Fig. 4(b) show the typical PP curves of equiaxed and precipitated microstructures in artificial seawater with different pH value. It is found that electrochemical behaviors for both microstructures based on the polarization curves are similar at each pH value, and the anodic polarization curves do not exhibit a typical active-passive characteristic [9, 15]. When the artificial seawater is in acidic/neutral condition, with the increase of pH values, we found: (i) corrosion potentials (E_{corr}) of both microstructures are shifted towards higher value, (ii) corrosion current density (j_{corr}) decreases to a lower level at the pH value of 7.06 (1.400 μA/cm^2 and 2.430 μA/cm^2 for the equiaxed and precipitated microstructures), and (iii) precipitated microstructure under each pH condition presents a much lower E_{corr} and higher j_{corr} in comparing to equiaxed microstructure, especially at the pH value of 1.19 (-0.579 V and 5.870 μA/cm^2 for E_{corr} and j_{corr}). This indicates the inferior self-passivating behavior and corrosion resistance of the precipitated microstructure in artificial seawater. Beacuse the electrolyte is under an alkaline condition, the PP curves indicate a much weaker spontaneous passive ability. These results are consistent with those from the OCP tests (Fig. 3(a) and Fig. 3(b)), indicating that the local

breakdown or dissolution of passive film has occurred on the surface [14, 15].

It is well known that the change of polarization curves reflects the different corrosion reactions. Cathodic polarization curve shows hydrogen evolution reaction caused by electrolyte reduction, oxygen reduction and the formation of OH groups, whereas anodic polarization presents a typical anodic dissolution reaction and the formation of passive oxide layer [27]. According to the literature [27, 35], during the formation of passive layer on Ti alloy surface which does not contain chlorine ions in electrolyte, the transition of ions from metal matrix to the passive reaction interface and the formation of passive film have the following reactions [28, 39]:

$$Ti \rightarrow Ti^{4+}+4e^{-} \quad (1)$$

$$H_2O \rightarrow O^{2-} + 2H^{+} \quad (2)$$

$$Ti^{4+} + 2O^{2-} \rightarrow TiO_2 \quad (3)$$

The reaction between cathodic oxygen and anodic dissolution in the chlorine ions solution is a complex process. It was reported that polarization curve for a non-oxidized Ti sample at low potentials corresponds to the anodic dissolution [9, 10]. Then non-stoichiometric titanium dioxides are generated with a low solubility, which can be expressed using the following reaction [28, 40]:

$$Ti^{3+} + xH_2O \rightarrow TiO_x + 2H^{+} + (2x-3)\, e^{-} \quad (4)$$

With the further polarization in a positive potential, the formation of unstable titanium oxychloride occurs according to the following reaction [11, 28, 40]:

$$TiOx + 2Cl^{-} \rightarrow TiO_xCl_2 + 2e^{-} \quad (5)$$

Based on the above corrosion analysis combined with polarization reaction, the formation of passive film on the Ti-1300 surface in the artificial seawater can be divided into three stages. In the first stage, titanium compounds (such as Ti suboxides of Ti_2O_3 and TiO, as well as TiOOH) are

formed as insoluble products, and can be adsorbed on the surface of the alloy. In the second stage, titanium oxidates are transformed from a less stable Ti_2O_3 into the stable TiO_2. In the third stage, the oxide layer is thickened with the polarization in the positive direction, and is consisted of Ti dioxide and Ti suboxides (such Ti_2O_3 and TiO).

In order to evaluate the corrosion resistance of this spontaneously formed passive system, the different corrosion parameters (such as E_{corr} and j_{corr} as listed in Table 2) were calculated using the Stern-Geary method [28] based on the PD curves. E_{corr} is defined as the potential at which the sign of current is changed during the cathodic to anodic potential sweep, and j_{corr} can be obtained directly by extrapolating the anodic and cathodic Tafel lines to the open-circuit corrosion potential (E_{corr}) [10, 28]. The polarization curves for both microstructures exhibit an obviously passive region, meaning that the formed oxide layer on the surface is stable and protective. Due to the pitting corrosion induced by the concentrated Cl^- ions, the corrosion resistance of both microstructures in the artificial seawater with the pH value of 1.19 is poorer those of the others, and the lowest E_{corr} (-0.579 V) and the highest j_{corr} (5.870 μA/cm^2) are obtained for precipitated microstructure. This is because that the precipitated microstructure is more susceptible to corrosion attack due to the formation of numerous microgalvanic cells, which accelerates pitting process. The different composition of α and β phases causes microgalvanic reactions for Ti-1300 alloys, which results in preferential corrosion of α phase and α/β interphase boundaries.

3.2.3 EIS measurement

Fig. 5(a) and Fig. 5(c) show the Nyquist plots of equiaxed and precipitated microstructures in artificial seawater, while Fig. 4(b) and Fig. 4(d) display Bode plots of the corresponding impedance spectra. Nyquist plots demonstrate that all the samples exhibit a depressed capacitive

semicircle with much larger diameter in the high frequency region followed by a straight line in the low frequency region. The capacitive-like semicircle is related to the complete passive barrier layer, and the larger diameters of capacitive semicircles imply that more protective passive films have formed on the surface [8, 41]. As shown in Fig. 5(a) and Fig. 5(c), the capacitive loop shrinks with further increasing of Cl^- ions in the artificial solution, and the radius of the semicircle is substantially decreased. This phenomenon indicates that the charge-transfer resistance becomes less important in the corrosion process with the increase of Cl^- ions [14, 42].

As shown in Fig. 5(b) and Fig. 5(d), both the impedance module (Z) and phase angle (θ) of precipitated microstructure are lower than those of equiaxed microstructure, which indicates a weaker electrochemical behavior for the precipitated ones. However, all the absolute impedance curves in a high frequency regime (10^4 - 10^5 Hz) are almost independent of frequency, implying the effect generated from solution resistance (R_s) [19]. With reducing of the frequency, the absolute impedance is firstly increased with a constant slope in the frequency of 10^1-10^4 Hz, but with different slope in frequency of 10^{-1} - 10^1 Hz. At the lowest frequency of 10^{-1} Hz, the absolute impedance is reduced with further increases of Cl^- concentration, the corresponding Bode plots in phase angles for both microstructures are also shifted to a value between -75° and -40°, indicating the decreased capacitive influence in the electrochemical behavior of the electrode [43]. The larger diameters of capacitive semicircles and the increased phase angle imply that more protective passive film has formed on the surface of equiaxed microstructure.

In general, the impedance response for electrochemical systems reflects a distribution of reactivity that is commonly represented in equivalent electron circuits as a constant-phase element (CPE) [44]. Polarization resistance (R_p) can be used to evaluate the corrosion resistance, which

requires to fit the EIS spectra using the equivalent circuit. In this study, the equivalent electron circuit with one time constants (Fig. 5(e)) is constructed to fit this impedance, which consists of the parallel combination terms (R_fQ) in series with the Ohmic resistance (R_e) [44, 45]. R_e is the Ohmic resistance and R_f is the charge transfer resistance. The CPE parameters α and Q are independent of frequency. A CPE was used to improve the fitting quality instead of the ideal capacitance due to the distribution of relaxation times originating from the surface heterogeneity. Independent of the cause of CPE behavior, the phase angle associated with a CPE is independent of frequency. The impedance of *CPE* (Z_{CPE}) can be expressed as [35]:

$$Z_{CPE} = \{Q(jw)^{\alpha}\}^{-1} \quad (6)$$

where j is the imaginary number, w is angular frequency, and α is a factor accounting for the deviation from the ideal capacitive behavior due to surface in homogeneity, roughness factors and adsorption effects. When $\alpha = 1$, it is assumed to be an ideal capacitor with the value of Q equals to the capacitance (C). For $\alpha < 1$, the Q cannot represent the capacitance. Both the Brug formulas and the Hsu and Mansfeld formula have been widely used to extract effective capacitance values from CPE parameters for studies on passive films, protective coatings, and corrosion inhibitors [46, 47]. By considering a normal time-constant distribution of the surface layer, Brug et al. proposed Eqs.7 for developing the relationships between interfacial capacitance and CPE parameters for both blocking and Faradaic systems. The result is demonstrated in Fig. 5(e), where a normal distribution of time constants results in a distributed time-constant behavior, which can be expressed as a summation of impedances. The effective capacitance associated with the CPE can therefore be expressed as [44]:

$$C_{eff} = Q^{1/\alpha}(R_e+R_f)^{(1-\alpha)/\alpha} \quad (7)$$

For passive alloys in relatively concentrated solutions, $R_f >> R_e$, Eq. 7 can be simplified to become Eq. 8.

$$C_{eff} = Q^{1/\alpha} R_f^{(1-\alpha)/\alpha} \quad (8)$$

Based on above model, the impedance (Z_ω) of electrode and its polarisation resistance ($R_{p\text{-}EIS}$) can be calculated using the following expressions [22, 35]:

$$Z_\omega = (R_f^{-1} + Q(jw)^\alpha)^{-1} \quad (9)$$

Polarization resistance ($R_{p\text{-}EIS}$) is given as [35]:

$$R_{p\text{-}EIS} = \lim_{\omega \to 0} (Z_\omega) = R_f \quad (10)$$

Based on the above equivalent circuits, the calculated impedance parameters are listed in Table 3. Obviously, the good quality of fitting results judged by the quite small chi-square values suggests the validity of the obtained parameters [36]. The precipitated microstructure has lower passive film resistance (R_f) and higher capacitance (C_{eff}) than the equiaxed microstructure at each pH, indicating the formation of thinner and unstable passive film on the surface. The weakening corrosion resistance for the precipitated microstructure, which may be contributed to the large number of detrimental microgalvanic cells formed between precipitated α_s and adjacent β phase. In addition, it is obvious that R_f is decreased with the increase of the Cl^- concentration (pH value), which demonstrates the deterioration effects caused by Cl^-. However, it is noted R_f value of the equiaxed microstructure are always higher than that of precipitated microstructure at each pH value indicating the superior corrosion resistance, which is in accordance with the results of OCP measurements and PP tests. $R_{p\text{-}EIS}$ values for precipitated and equiaxed microstructures at various pH values can be obtained by using the Eq (10) from Table 3. $R_{p\text{-}EIS}$ for precipitated microstructure in seawater solutions with pH values of 1.19, 4.22 and 9.54 are decreased to 95.68 kΩ·cm^2, 120.96

kΩ·cm^2 and 113.53 kΩ·cm^2, respectively, which are two and three times lower than those for the solutions with a pH value of 7.06 (204.69 kΩ·cm^2). It indicates that the passive film becomes much thinner and more porous after adsorption of Cl^- ions, thus results in the deterioration of the corrosion resistance. Cl^- ions not only inhibite the reactivity of the interfacial charge transfer, but also decrease the pitting potential and significantly accelerates the chloride-induced localized corrosion [9, 28, 48, 49]. Therefore, the appearance of α_s phase and corrosive ions (Cl^-) results in the weak corrosion resistance for Ti-1300 alloy in artificial seawater.

3.2.4 XPS analysis

The alloys subjected to immersion of 24 h in artificial seawater (pH = 7.06), were selected to characterize surface chemical nature of native passive film using XPS. Fig. 6 and Fig. 7 show the high-resolution XPS spectra of Ti 2p, O 1s, Al 2p, Mo 3d, V 2p and Cr 2p recorded at the outermost passive film for both microstructures with different sputtering depths. The native passive films for both microstructures have the same composition, including Ti, Al, Cr and O. The content of Ti increases and that of O rapidly decreases with the increasing sputtering depths, and then becomes equal to each other. According to the peak intensity in high-resolution XPS signals of Ti $2p_{3/2}$, Al $2p_{3/2}$ and Cr $2p_{3/2}$, the main component of passive film is TiO_2 with Ti^{4+} at 459.1 eV, Ti_2O_3 with Ti^{3+} at 457.4 eV, TiO with Ti^{2+} at 455.1 eV, Al_2O_3 with Al^{3+} at 74.3 eV, Cr_2O_3 with Cr^{3+} at 576.9 eV and Cr suboxides with neglectable content with reference to the NIST XPS database [50].

The outermost layer is identified as the mixed oxides of TiO_2, Al_2O_3 and Cr_2O_3 for both microstructures, and these oxides have the highest stability due to thermodynamic reasons [10, 51]. With an increasing sputtering depths, the peaks are shifted toward the low binding energy and Ti

$2p_{3/2}$ peak is boarder than that of pure TiO_2, suggesting that abundant sub-oxides are present beneath the outer TiO_2 layer. These are mainly Ti_2O_3 and TiO as the oxidation state of Ti is gradually decreased from Ti^{4+} through Ti^{3+} and Ti^{2+}. When the sputtering time is increased to 60 s, some spectra of Ti $2p_{3/2}$, Cr $2p_{3/2}$ and Al $2p_{3/2}$ for equiaxed microstructure are still retained, while only some suboxides of Ti and Al are detected for precipitated microstructure. When the sputtering time exceeds 120 s, the spectra of suboxides and Al_2O_3 are detected for equiaxed microstructure, while the precipitated one only exhibits peaks of pure metal elements. The thickness of passive film can be obtained based on the sputtering depths from the XPS spectra. When the sputtering time is given to 1s, the sputtering depth is approximately 0.1 nm for titanium alloy according to the literature [10, 52]. In this study, the film thicknesses for equiaxed and precipitated ones in artificial seawater can be calculated to be 8-10 nm and 4-6 nm, respectively. In precipitated microstructure, the acicular α_s platelets on the β matrix obviously weaken the passivation ability of the alloy due to the potential difference, which induces microgalvanic cells and accelerates pitting reaction [5, 13].

3.3 Surface topography characterization

Fig. 8 shows the variation of weight loss of precipitated and equiaxed microstructures as a function of immersion time in 5 M HCl solution. The variation of weight-loss with immersion time shows a linear trend, indicating corrosion rate for both microstructures is nearly constant [13]. Precipitated microstructure has been heavily attacked by Cl^- ions and exhibits an inferior corrosion resistance. The weight loss rate of precipitated microstructure (~ 0.0043 g/cm^2) is much higher than that of equiaxed microstructure (~ 0.0012 g/cm^2), meaning that precipitated microstructure has poor corrosion resistance. These differences can be attributed to microstructure characteristics,

and α_s phase is the preferential dissolution location due to its low content of anodic alloying elements.

The immersed surfaces for both microstructures are all initially mirror-like finishes on visual inspection. In the case of immerse in 5 M HCl solution, the entire surface for precipitated microstructure is rapidly darkened due to the preferential corrosion of α_s phase, but the surface of the equiaxed microstructure exhibits no marks of corrosive traces, with only silvery white surface observed. Fig. 9 and Fig. 10 show the SEM images of the detailed surface morphologies for both microstructures after immersed for different time. As the immersion time is not exceeded to 4 days, the uniform corrosion process is observed on both microstructures, and the remarkable selective corrosion is caused by the concentration of Cl^- ions at higher immersion time (longer than 5 days). For the equiaxed microstructure, the corroded surface is covered with evenly distributed corrosion pits and equiaxed β grain. When immersion time is increased to 2 day, the surface has been slightly attacked and a small quantity of corrosion pits is formed on the grain boundaries and grain interiors. The zoomed-in image of a local area for pit morphologies is also inserted in Fig. 9. With the immersion time up to 4 days, only enlarge corrosion pitting is identifiable, and the sizes of pit cavities are increased to approximately 3~8 μm. When the immersion time is increased to 8 days, the sample has been heavily attacked and the entire surface is covered with numerous cusps and cavities with sizes of 10~20 μm. Both grain boundaries and grain interiors are attacked, but more aggressive attack is occurred at grain boundaries. Moreover, localized corrosion occurred on selective grains in the equiaxed microstructure. A large portion of grains and grain boundaries were only slightly attacked.

For precipitated microstructure, the remarkably uniform corrosion associated with active

dissolution was observed after 2 day immersion (Fig. 10(a)). The surface has been seriously eroded, which is covered with numerous cusps and cavities and exhibits a honeycomb morphology. The preferential area for the aggressive attack is grain boundaries and α_s phases, and the size of the cavities is much larger than 15 μm. The zoomed-in image of the cavities located at grain boundaries and grain interiors is chartered and inserted in Fig. 10. With further increment of immersion time (Fig. 10(b)), the corroded cavities with much larger areas and greater depth are randomly distributed over the surface, indicating precipitated microstructure presents worse corrosion resistance ability. Fig. 10(c) and Fig. 10(d) show the serious surface degradation after 8 day and 12 day immersion. The surface undulation is sharply increased and has much higher roughness values. Moreover, the detailed microstructure analysis at the bottom of eroded cavities confirmed that the preferential dissolution locations for precipitated microstructure would be concentrated on α_s phase and α+β interphase boundaries. The difference in the composition between α_s and β phase causes the generation of microgalvanic reaction, which result in the preferential corrosion of α_s phase and α/β interphase boundaries.

According to the above results, the corrosion rate for precipitated microstructure is much higher than that of equiaxed microstructure, which indicates its weaker corrosion resistance and passive behavior. Fig. 11 shows the schematic diagram of microgalvanic cell formed between acicular α_s and adjacent β phase in the precipitated microstructure. In the initial stage (Fig. 11(a)), the whole surface of precipitated microstructure can rapidly form a continuous passive film, which leads to a rapidly positive shift of the OCP. The conductive circuit has not been formed because of the insulated oxide layer. With elongated immersion time duration (Fig. 11(b)), many corrosive ions (such as Cl^-) will diffuse and accumulate in the film/solution interface from electrolyte

solution, and thus the passive film has been heavily attacked. The local breakdown or dissolution of passive film has occurred, which promotes corrosive solution infiltrating into the crevice at film/matrix interface. Moreover, the potential difference (ΔE) between oxide layer and Ti matrix is increased. But because of the effective protection of the passive layer, the galvanic corrosion keeps a steady process and then gradually slows down in this period. At the last stage (Fig. 11(c)), the passive film layer has been completely dissolved and removed, and the substrate is also completely exposed to electrolyte solution, which accelerates the galvanic corrosion between acicular α_s and adjacent β phase. Moreover, ΔE has been increased dramatically, i.e., resulting in an enhancement of driving force for galvanic corrosion. The galvanic current density (I) also increases rapidly and the weight loss is much higher than that in the initial. It is well known that severe pitting corrosion occurs with a large galvanic current density, and thus the effect of metastable pits on the corrosion process cannot be ignored. In this acceleration stage of galvanic corrosion, the nucleation of the pitting in α_s phase and α/β interface can occur at potentials well below the pitting potential, and this nucleation can result in the propagation of the metastable pit. When the pit nucleates at the site, the high reaction rate within the pit will cause a high chloride concentration, which accelerates the galvanic corrosion and enlarge the pit in depth. Therefore, the corrosion mechanism of precipitated microstructures can be explained by the passive behavior, microgalvanic corrosion and pitting.

3.4 Mechanical properties degradation

Typical engineering stress-strain curves of equiaxed and precipitated microstructures after different immersion times are shown in Fig. 12(a) and Fig. 12(c), and the corresponding mechanical properties are summarized in Fig. 12(b) and Fig. 12(d). Significant difference can be

noted in the curves for both types of microstructures after different immersion time. Precipitated microstructure after immersion 14 and 20 days is broken without apparent necking at a very low strain of 0.015, and equiaxed microstructure in different immersion time all show more obvious uniform elongation and necking. When the immersion time is increased to 2 days, ultimate tensile strength (UTS) and elongation (E) of the equiaxed microstructure are 950 MPa and 14.5 %, whereas the precipitated microstructure exhibits a high UTS of 1679 MPa and a low E of 2.8 %. When the immersion time is increased to 20 days, the mechanical properties for both microstructures are all deceases significantly.

Based on the above results, it is found that the UTS and E values of both microstructures decrease gradually with the increase of immersion time. Moreover, a much severe degradation of mechanical properties is obtained for precipitated microstructure, implying severe degraded mechanical properties are generated due to the formation of the detrimental microgalvanic cells. The degradation of mechanical properties with increasing immersion time can be mainly attributed to two primary factors. Firstly, many large and deep pitting cavities increase the surface defect, which may act as the crack tip during the deformation. Secondly, hydrogen embrittlement is occurred in the pitting cavities, which is caused by the diffusion of hydrogen ions from the corrosion solution. Therefore, the stability of mechanical properties for Ti-1300 alloy is degraded with the increasing of immersion time, and precipitated microstructure exhibits a more severe mechanical degradation due to nano-scale α_s precipitates.

Fig. 13 and Fig. 14 show SEM images of the fracture surfaces for both microstructures ruptured under the immersion time of 8 and 20 days. For the equiaxed microstructure (Fig. 13), the fracture feature is mainly consisted of shear-lip zone at the edge region, as well as the crack

propagation zone in the central region. At a higher magnification, the central region exhibits a large number of dimples and cleavage fracture planes surrounded by tearing ridges, and some large and deep equiaxed dimples are present, exhibiting more ductile deformation features. On the contrary, the fracture surface near the edge region consists of the mixture of shallow and parabolic dimples, which belong to shear dimples and form under shear stress in the shear-lip zone (Fig. 13(b) and Fig. 13(d)). For equiaxed microstructure, the transgranular fracture and occasional interfacial decohesion between β grains indicate that dimple rupture leads to ductile fracture. When the immersion time is increased to 20 days, the exposed surface has been evidently attacked by the Cl^- ions in the solution, and the shear-lip zone in the outer periphery is smaller than that with immersion time of 8 days. The fracture surface in the crack propagation zone consists of a rugged area surrounded by the ligaments of ductile tearing (Fig. 13(c)), and the outer surface is covered with numerous cusps and cavities with sizes of 10~20 μm located on grain boundaries (Fig. 13(d)).

For precipitated microstructure, the fracture feature reveals a mixture feature of cleavage planes and staircase-like morphology, the grain boundary can be also observed (Fig. 14). The fracture occurred preferentially along the prior β grain boundaries, and the cavities are nucleated and propagated at the interface between the prior β grains. This appearance of both coarse and fine boundary facets indicates the enhanced embrittlement, and ultimately leads to poor ductility. In addition, the fracture surfaces show an increase in the fraction of brittle area with increasing immersion time. The fractographs shown in Fig. 14(c) and Fig. 14(d) reveals inter-crystalline fracture and occasional interfacial decohesion between β grains, and that the tearing ridges lie on the individual facets of β grains. The higher magnification shows that the dimples in the shear-lip

zone become slightly larger as the immersion time increases from 8 days to 20 days. This result indicates that the Cl^- concentration significantly affects the cavity nucleation and growth, and these cavities lead to the degraded mechanical properties. Therefore, the absence of mixed features of cleavage planes and staircase indicates the brittle fracture mode for precipitated microstructure, which exhibits the inferior mechanical degradation due to the precipitated α_s phase.

4. Conclusion

(1) In precipitated microstructure, precipitates of α_s phase with an acicular shape around 40 ~ 60 nm in width are distributed inside the β grain, which restricts the growth of other α_s phase due to pinning effect.

(2) Both of equiaxed and precipitated microstructures exhibit spontaneous passivity behavior without obviously active-passive characteristics due to the formation of passive films. XPS results demonstrate that this passive layer is mixed oxides of TiO_2, Al_2O_3 and Cr_2O_3.

(3) The α_s precipitates act as the preferential dissolution locations, where "microgalvanic cells" with their adjacent intergranular β phases can be formed to accelerate pitting reaction. The formed microgalvanic cells as well as pitting reactions are identified as the main factor affecting the corrosion performance of Ti-1300 alloy.

(4) The mechanical properties are degraded lineally with immersion time due to pitting reaction. The precipitated microstructure exhibits a much severe mechanical degradation behavior, which is mainly because abundant corrosion cavities are nucleated and propagated at α_s precipitates and prior β grains interface.

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